

RARE-EARTH PEROVSKITE COLLOIDAL DISPERSION AND METHOD
FOR THE PRODUCTION THEREOF

The present invention relates to a colloidal dispersion
5 of a rare-earth perovskite and to its process of
preparation.

Colloidal dispersions, or sols, of rare-earth compounds
are known, especially rare-earth oxides, which may for
10 example be of great use in catalysis applications.
However, at the present time, there are no colloidal
dispersions of rare-earth compounds in perovskite form.
Such dispersions could be of interest in various
applications, for example in catalysis, in magnetism or
15 in materials for the electrodes of fuel cells.

It is an object of the invention to provide such a type
of product.

20 The subject of the invention is a colloidal dispersion
of a rare-earth compound characterized in that the
rare-earth compound is in the form of colloids having a
perovskite structure of formula:



25 in which:

- Ln is at least one rare earth other than just cerium;
- B is at least one element chosen from the group comprising elements of atomic number from 22 to 31,
30 from 40 to 51, from 73 to 83 and aluminum.

The invention also relates to a process of preparing a
dispersion as defined above, which is characterized in
that it comprises the following steps:

- 35 - a perovskite of formula (1), having the form of
elementary crystallites at most 500 nm in size, is
brought into contact with a monovalent acid having a
pKa of between 2.5 and 5.0;

- the mixture obtained is heated to a temperature of between 50°C and 200°C; and

- if necessary, the reaction mixture obtained is purified.

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Perovskites obtained in colloidal form offer various advantages: they are nanoscale products with a specific surface area of interest for catalysis; they provide raw materials that can be used for producing O²⁻ ion
10 exchange membranes or films; and these dispersions can constitute electrorheological or magnetorheological fluids.

Other features, details and advantages of the invention
15 will become more fully apparent on reading the following description and from the various specific but nonlimiting examples intended to illustrate it.

In the rest of the description, the term "perovskite"
20 must be taken in the wide sense to denote any compound of chemical formula (1) given above and having a perovskite-type crystallographic structure. The expression "colloidal dispersion or sol of a rare-earth compound" denotes any system consisting of fine solid
25 particles with colloidal dimensions based on a rare earth, with the perovskite structure, in suspension in a liquid phase, it being possible for said particles furthermore to optionally contain residual amounts of bonded or adsorbed ions, such as for example acetates,
30 citrates, nitrates, chlorides or ammonium or sodium ions. The percentage X of these bonded or adsorbed ions, expressed as the molar ratio X/Ln, may vary between 0.01 and 1.5, more particularly between 0.01 and 0.6, it being understood that these values are
35 given merely by way of example. The dispersion may also contain residual amounts of compounds of the following type: Ln₂O₃, Ln(OH)₃, LnCO₃, Ln(acetate)₃, SrCO₃, BaCO₃, CaCO₃, MgCO₃ or B_vO_w, optionally in colloidal form. It should be noted in such dispersions that the rare earth

may be either completely in the form of perovskite colloids, or simultaneously in the form of perovskite colloids and of other various forms that are dissolved, of the Ln^{3+} ion or $\text{Ln}_x\text{OH}_y^{t+}$ polyion type.

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The term "rare earth" is understood to mean the elements of the group formed by yttrium and those elements of the Periodic Table having atomic numbers between 57 and 71 inclusive.

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The first subject of the invention is a colloidal dispersion based on a rare earth, with the perovskite structure described above, corresponding to formula (1). In this formula, Ln denotes a rare earth or several rare earths in combination, the case of cerium as the only rare earth present being excluded. The rare earth may more particularly be lanthanum or lanthanum in combination with cerium. In the case of a lanthanum/cerium combination, the $\text{La}/(\text{La} + \text{Ce})$ atomic ratio is preferably at least 0.5 and more particularly at least 0.7.

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The element B, which is chosen from elements having atomic numbers from 22 to 31, from 40 to 51, from 73 to 83 and aluminum, may more particularly be iron, manganese, cobalt, nickel, ruthenium, chromium, palladium, platinum and copper. The invention applies most particularly to the case when B is iron, manganese or cobalt. B may be a combination of the aforementioned elements. In the case of a combination, the combined elements are preferably of different valences. One example that may more particularly be mentioned is the iron/cobalt combination.

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35 The perovskite of formula (1) may be doped. By this it is meant that the rare earth Ln may be partly substituted with a monovalent or divalent cation. This cation may be chosen from alkali metals and alkaline-earth metals. More particularly, the cation may be

sodium, potassium, lithium, calcium, magnesium, strontium and barium. Strontium is a preferred dopant. The products thus doped may have improved catalytic properties.

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The amount of substituting cation is generally at most 50% and may for example vary between about 1% and about 50%, this amount being expressed through the cation/(cation + Ln) atomic ratio.

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Examples of compounds constituting the dispersions of the invention that may be mentioned include those of formula: LaMnO_3 , $\text{LaMn}_{1-y}\text{Cu}_y\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$, LaCoO_3 , $\text{La}_{1-x}\text{Sr}_x\text{CoO}_3$, LaFeO_3 , $\text{La}_{1-x}\text{Sr}_x\text{FeO}_3$, $\text{La}_{1-x}\text{Ce}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$,
15 $\text{LaFe}_{1-u-v}\text{Co}_u\text{Pd}_v\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-u-v}\text{Co}_u\text{Pd}_v\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-u}\text{Pd}_u\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-u}\text{Pd}_u\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{Fe}_{1-y}\text{Co}_y\text{O}_3$, $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Ni}_y\text{O}_3$, LaCrO_3 , LaNiO_3 , LaCuO_3 , LaAlO_3 , PrCoO_3 , PrMnO_3 and $\text{Sm}_{1-x}\text{Sr}_x\text{CoO}_3$.

20 The well-crystallized perovskite structure of the colloids of the dispersions of the invention can be observed by X-ray diffraction. This crystallized perovskite structure may for example be demonstrated by X-ray diffraction on solid colloids recovered either by
25 drying the colloidal dispersions at low temperature ($T < 60^\circ\text{C}$) or by ultracentrifuging them.

The sizes of the colloidal particles making up the sols of the invention may vary widely. Thus, the particles
30 may have a mean diameter of at most 500 nm, more particularly at most 200 nm and lying especially between 5 and 200 nm, more particularly between 5 and 30 nm and even more particularly between 5 and 20 nm. This diameter is determined by photometric counting on
35 the basis of analysis by HR-TEM (high-resolution transmission electron microscopy) or by cryo-TEM (cryogenic transmission electron microscopy). This technique is used to observe the specimens kept frozen in their natural environment, which is either water or

an organic solvent. The freezing operation is carried out on thin films about 50 to 100 nm in thickness either in liquid ethane in the case of aqueous specimens or in liquid nitrogen in the case of the
5 others.

The colloids may furthermore be monodisperse in size.

They may also have various morphologies.

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In general, the morphology is of isotropic type, that is to say the colloids have a ratio $m = L/I$ of less than 3, L representing the greatest length and I the smallest dimension (width or thickness).

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The morphology may of anisotropic type, that is to say the colloids have an m ratio of greater than 5, more particularly greater than 10 and even more particularly greater than 25. Anisotropic morphologies may be
20 exhibited by colloids in the form of platelets or fibers. It should be noted here, and throughout the rest of the description, that it is in the case of colloids having an anisotropic morphology that they generally have the largest size, that is to say one
25 lying within the range between 200 nm and 500 nm.

The dispersions of the invention have a pH value that may vary within a certain range. For example, they may have a pH value of between 4 and 8.5, preferably
30 between 4 and 6.5.

The dispersions of the invention may have a concentration within a wide range, for example a concentration of at least 5 g/l, preferably a
35 concentration of at least 100 g/l, this being expressed by weight of perovskite.

Finally, the dispersions according to the invention may be aqueous dispersions - the continuous phase being

water - or dispersions in a continuous phase that may be formed by a water-miscible organic solvent/water mixture or else dispersions in a water-miscible organic solvent.

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Examples of solvents that may be mentioned include: alcohols, such as methanol or ethanol; glycols, such as ethylene glycol; acetate derivatives of glycols, such as ethylene glycol monoacetate; ethers of glycols; 10 polyols; and ketones.

The dispersions, according to the preferred embodiments of the invention, are stable dispersions with no settling over periods of longer than six months.

15

A process of preparing a dispersion of the invention will now be described.

As indicated above, this process includes a first step 20 in which a perovskite of formula (1) is brought into contact with a specific acid.

As perovskite, any crystallized perovskite satisfying formula (1) may be used. However, the size of the elementary crystallites or of the organized domains of 25 this perovskite must be at most 500 nm, especially at most 200 nm. This size must preferably be at most 100 nm, advantageously at most 40 nm and even more advantageously at most 30 nm. A crystallite size of at 30 most 500 nm or 200 nm is needed in order to be able to obtain a colloidal dispersion, and the size of the colloids will be smaller the smaller the size of the initial perovskite crystallites.

35 Here and throughout the description, it should be pointed out that the size of the elementary crystallites or organized domains is determined in a known manner from X-ray diffraction diagrams. This determination may thus be carried out on the first peak

of significant intensity at low angle. More precisely, this first low-angle peak corresponds to a 2θ of about 23° for $\text{Cu}(K\alpha + K\beta)$ radiation or interlattice distances of around 3.8 to 4.0 Å. These values are, for example,
5 3.87 Å for LaMnO_3 , 3.92 Å for LaFeO_3 and 3.82 Å for LaCoO_3 .

The crystallite size is then calculated in a known manner using the Scherrer equation, which takes the
10 mid-height width of the peak into account.

Such a perovskite may be prepared by any means known to those skilled in the art. Mention may be made of perovskites prepared by processes carried out at low
15 temperature involving wet precipitation, followed by calcination, or at high temperature involving flame combustion processes and gas phase reactions.

In the particular case of the preparation of
20 dispersions with colloids having anisotropic morphology, this starts with a perovskite of anisotropic morphology. Such a perovskite may be prepared by using, for example, an anisotropic oxide, especially MnO_2 of anisotropic morphology, or else an
25 Fe oxyhydroxide of αFeOOH type of anisotropic morphology. For example, it is possible to use an MnO_2 oxide of anisotropic morphology, as described in the article by Xun Wang and Yadong Li, Chem. Eur. Journal, 2003, 9, No. 3, pages 300-306 for obtaining $\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$.

30 The acid with which the perovskite is brought into contact is a monovalent acid having a pKa of between 2.5 and 5.0. Preferably, this acid is a water-soluble acid. Suitable acids within the scope of the invention
35 that may be mentioned include: acetic acid, formic acid, propionic acid and monochloroacetic acid. Acetic acid may most particularly be used.

The contacting operation usually takes place in aqueous

medium with a solution of the acid in order to obtain a suspension.

5 The concentration of the acid in the solution is not critical and it can vary widely. However, this concentration is preferably chosen so that the suspension obtained can also constitute a liquid phase that is sufficiently extensive to achieve attack under proper stirring conditions during the next, heating
10 step of the process. Thus, this concentration may be between 0.05M and 5M.

The amount of acid used is generally such that the H^+ /perovskite molar ratio is between 0.05 and 20, more
15 particularly between 0.05 and 5. In fact, this amount must be chosen so that the attack, which takes place during the process, of the perovskite by the acid is a controlled attack. Too small an amount of acid runs the risk of not being able to obtain a colloidal
20 dispersion, whereas too large an amount runs the risk of forming too many ionic species. The acid contacting step is usually carried out at ambient temperature, that is to say between 15°C and 25°C. It may also be carried out by adding the perovskite to an acid
25 solution, or else by putting the perovskite into suspension in water and then adding the acid in suitable amounts.

According to a variant of the process, the perovskite
30 may be milled before it is brought into contact with the acid. Various milling operations may be used, for example air-jet dry milling or preferably wet milling, for example using a ball mill. The balls of the mill may be made of Al_2O_3 or zircon, having a mean size
35 centered on about 0.2 to 1.0 mn, preferably 0.2 to 0.8 mn. The milling time may vary from 2 min to 45 min.

The second step of the process consists in subjecting the mixture obtained after the first step to a heat

treatment. This heat treatment allows the perovskite to be attacked by the acid and is carried out by heating to a temperature of between 50°C and 200°C. This treatment may be carried out in a closed vessel, for example in a closed reactor of the autoclave type. The temperature of the heat treatment depends on the solubility of the initial perovskite. This temperature may also be adapted according to the acid concentration and to the H^+ /perovskite ratio of the solution used in the first step.

The duration of the treatment can vary, this being shorter the higher the temperature.

The optional next step of the process is a purification step. The purpose of this is in fact to remove the ionic species and/or parasitic colloidal particles present in the suspension obtained after the heat treatment.

This step may be carried out in various ways depending on the type of suspension resulting from the heat treatment.

In certain cases, it is possible to obtain a colloidal dispersion directly after this treatment. However, in such cases, purification is worthwhile in order to increase the stability of the dispersion. This purification may be carried out in particular by ultrafiltration. The dispersion is ultrafiltered over a 3KD membrane for example. The purification then takes place by dilution with demineralized water and concentration by ultrafiltration. The purification is carried out until the necessary reduction in ionic force is achieved, so as to obtain a stable colloidal dispersion.

It is also possible to purify the dispersion using a resin.

It is preferable to use an anionic resin in combination with a cationic resin.

- 5 The resin treatment is carried out in any suitable manner. The resins may be brought into direct contact with the colloidal dispersion.

10 In other cases, when what is obtained directly after the heat treatment is not a colloidal dispersion but a suspension of a solid in an aqueous liquid phase, the solid product is separated from the reaction mixture. This separation may be carried out by any known technique, for example by filtration, settling or
15 centrifugation.

The solid thus obtained can then be resuspended in a liquid medium, for example water, so as to give the dispersion of the invention. These
20 separation/redispersion operations may optionally be repeated if necessary. The dispersion obtained after resuspension in water may also be purified and/or concentrated by ultrafiltration or by treatment with a resin.

25 In the case of a dispersion partially or completely in a solvent medium other than water, this dispersion may be prepared from an aqueous dispersion, such as that obtained by the process that has just been described,
30 and by the addition of the organic solvent of the type mentioned above to this aqueous dispersion, followed by distillation in order to remove the water. A number of different variants of the process of the invention will now be described below. These variants relate to
35 various steps of the process and can be used individually or in combination. They have the common purpose of providing dispersions whose colloids have small mean diameters, lying within the 5 and 30 nm range and more particularly the 5 to 20 nm range.

The first variant relates to the initial perovskite used in the first step of the process. This perovskite may be prepared using a specific process. This process
5 uses, as starting products, salts of the elements Ln and B and, in the case of the preparation of a product based on a doped perovskite, one or more monovalent or divalent cations. The salts may be salts of inorganic or organic acids, for example of the sulfate, nitrate,
10 chloride or acetate type. It should be noted that nitrates and acetates are particularly suitable. As cerium salts, cerium^{III} acetate, cerium^{III} chloride or cerium^{III} or cerium^{IV} nitrate may more particularly be used, as may also mixtures of these salts such as
15 acetate/chloride mixed salts.

These salts are mixed in aqueous medium in order to form a preferred solution.

20 Next, the mixture is made to react with a base under basic conditions so as to obtain a precipitate.

As base, products of the hydroxide type may especially be used. Mention may be made of alkali metal or
25 alkaline-earth metal hydroxide and aqueous ammonia. Secondary, tertiary or quaternary amines may also be used. However, amines and aqueous ammonia may be preferred insofar as they reduce the risk of contamination by alkali metal or alkaline-earth metal
30 cations. Urea may also be mentioned. The base is generally used in the form of a solution.

The precipitation reaction takes place under basic conditions, that is to say at pH greater than 7,
35 preferably greater than 9. In the particular case of the preparation of doped perovskites, especially those doped with strontium, calcium and magnesium cations, this pH may be higher, for example at least 12.

The precipitate obtained as a result of the reaction is separated from the reaction mixture. This separation may be carried out by any known technique, for example by filtration, settling or centrifugation. The
5 separated product may for example be washed, being resuspended in water and then separated again. Next, the product obtained is calcined at a temperature of at least 450°C. This temperature may thus be between 450°C and 1200°C, more particularly between 500°C and 900°C.

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In general, this calcination is carried out in air.

The calcination time may for example be between 1 and 10 hours. This time is usually shorter the higher the
15 calcination temperature. The calcination temperature and time are set so as to be able to obtain a product having a perovskite structure the size of the elementary crystallites of which is small, that is to say preferably at most 60 nm, this size of the
20 elementary crystallites being determined by X-ray diffraction as indicated above. It should be noted that, according to one particular way of implementing the specific process for preparing the perovskite according to the first variant that has just been
25 described, the calcination may be a flash calcination. The term "flash calcination" is understood to mean the direct introduction of a product to be calcined into a furnace brought to temperature beforehand. Under these conditions, the rate of rise is instantaneous. One
30 example of industrial flash calcination is calcination in a furnace of the tunnel furnace type. In this case, the calcination temperature is higher than that given above. It may thus be between 800°C and 1200°C for a short time of only a few minutes, for example between 1
35 and 15 minutes. The perovskite thus obtained may then be milled as indicated above.

According to another variant of the process of the invention, an initial aqueous mixture of salts of the

elements Ln and B with a superstoichiometric Ln/B ratio is formed. Preferably, this superstoichiometry is set so that the Ln/B atomic ratio satisfies the relationship $1 < \text{Ln/B} \leq 1.25$.

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According to a third variant, during the reaction or after the reaction of the salts of the elements Ln and B with the base, and before calcination, at least one organic compound chosen from carboxylic acids, amino acids, polyacrylic acids and their salts and alkylamines is added to the reaction mixture or to the mixture after the reaction, respectively. When the organic compound is added during the reaction with the base, the organic compound may be introduced either into the base solution or into the solution of the salts of the elements Ln and B. In the case of two or more organic compounds being used, these may be added together or separately at different times.

20 As regards carboxylic acids, aliphatic monocarboxylic or dicarboxylic acids may especially be used and, among these, those that are saturated acids are more particularly used. It is also possible to use fatty acids and more particularly saturated fatty acids. Thus, lauric acid may especially be mentioned. As dicarboxylic acids, oxalic acid and succinic acid may be mentioned.

30 Among carboxylic acids, phenol acids such as salicylic acid may also be employed. Alcohol acids such as citric acid may also be used.

The salts of the aforementioned acids may also be used.

35 The amino acid may more particularly be an aliphatic amino acid, such as aminocaproic acid. This may also be a natural amino acid, such as lysine, arginine, alanine, aspartic acid and glutamic acid. Here again, the salts of these acids may also be used.

It is also possible to use polyacrylic acids and their salts, such as sodium polyacrylate and more particularly those having a weight-average molecular weight of between 2000 and 5000.

The amount of organic compound is preferably chosen so that the organic compound/perovskite molar ratio is between 0.1 and 1 when this compound is added during the reaction between the Ln and B salts and the base. When it is added after the reaction between the salts and the base, the amount of organic compound is preferably chosen so that the organic compound/perovskite mass ratio is between 1 and 60%. The mixture to which the organic compound has been added may optionally undergo a milling operation.

This milling may be carried out in various ways.

A first way consists in carrying out a high-energy milling operation of the wet milling type. Such milling is carried out on the wet precipitate obtained after the step of reaction with the base, the precipitate having been separated from the reaction mixture. The wet milling may be carried out for example in a ball mill.

A second way consists in carrying out a moderate-energy milling operation by subjecting a suspension of the precipitate to a shearing action, for example using a colloid mill or a turbine agitator. This suspension may be an aqueous suspension obtained by resuspending in water the precipitate obtained after the step of reaction with the base, followed by separation. This may also be the reaction mixture obtained directly at the end of this same step after the addition of the organic compound without the precipitate being separated from the liquid medium.

It is also possible to obtain a product in solid form from a dispersion according to the invention. To do this, the dispersion may for example be subjected to an evaporation, centrifugation, freeze-drying, ultra-
5 filtration or osmotic-compression operation.

Osmotic compression is a known method, the principle of which consists in balancing the chemical potential of water across a membrane.

10

A procedure involves putting the colloidal dispersion in a dialysis bag, for example made of a cellulose material, this bag being placed in an aqueous solution whose chemical potential of the water is different from
15 that of the aqueous phase of the dispersion. This may be accomplished for example by using an aqueous solution of polyethylene glycol (PEG) or of dextran. The PEG or dextran concentration sets the osmotic pressure and therefore the final concentration of the
20 colloidal dispersion. Evaporation, centrifugation and ultrafiltration may be carried out using any suitable device. Preferably, the dispersion is dried in an oven at low temperature, preferably at a temperature below 50°C, or by using a rotary evaporator.

25

The treatments that have just been mentioned are carried out individually or in combination and are used to pass in a continuous manner from a colloidal dispersion to a gel or a paste and then to a powder.
30 This paste or powder may optionally be dried.

This powder is redispersible, that is to say it can be resuspended in water and thus result in a colloidal dispersion according to the invention having the
35 characteristics described above.

The dispersions of the invention may be used in many applications. The colloids may be used as elementary constituents for production of catalysis materials,

especially for automobile post-combustion or for the oxidation of volatile organic compounds. The colloids may also be used as elementary constituents for production of materials for solid-state electrolytes
5 (membranes for controlled diffusion of O^{2-} ions and H^+ ions) or for fuel cell electrodes.

These perovskite colloids may also be used as nanoscale functional fillers in polymer-based coatings in order
10 to give these polymers various catalysis properties, electrical properties or magnetic properties. The composite coatings thus formed then develop antistatic or electromagnetic compatibility properties.

15 The dispersions may also be employed for manufacturing films.

These colloidal dispersions may also be used as raw materials for the production of electrorheological
20 fluids or as magnetorheological fluids.

Examples will now be provided.

EXAMPLE 1

25 This example relates to the preparation of an $LaMnO_3$ colloidal dispersion.

A manganese nitrate solution was obtained by dissolving 62.75 g of $Mn(NO_3)_2 \cdot 4H_2O$ (MW = 250.9, i.e. 250
30 millimoles of Mn) to which 500 cm^3 of demineralized water was added. A lanthanum nitrate solution was obtained by diluting 146.5 g of a 2.88M La lanthanum solution of 1.686 density with demineralized water so as to obtain 500 cm^3 of solution (i.e. 250 millimoles).

35 The manganese nitrate solution was mixed with the lanthanum nitrate solution.

The manganese nitrate/lanthanum nitrate solution thus

obtained was quickly added, at room temperature, to 650 cm³ of a 3M aqueous ammonia solution while stirring. A precipitate formed instantly. The pH of the suspension obtained was 9.5.

5

The suspension was centrifuged at 4500 rpm for 15 min. The pellet obtained was taken up in 1000 cm³ of demineralized water, and stirred for 30 min. After again centrifuging for 15 min, the solid obtained was
10 dried at room temperature for 16 hours. The solid was then dried further at 60°C for 10 hours.

The product was calcined at 800°C for 6 h.

15 After cooling, the perovskite structure LaMnO₃ (MW = 242) was determined by X-ray diffraction.

3.02 g of LaMnO₃ (12.5 millimoles) prepared as described above were added to 25 cm³ of 2M acetic acid,
20 the mixture being stirred for 20 min. The [acetic acid]/[perovskite] molar ratio was 4.

The mixture was transferred into a Teflon (PTFE) container inserted into a hydrothermal treatment cell
25 (Parr bomb). The hydrothermal treatment was carried out at 160°C for 16 hours.

After cooling, the supernatant phase was removed. The pellet was redispersed with stirring in 25 cm³ of
30 demineralized water. A colloidal phase and a solid were obtained. Colloids having a mean size of 35 nm were observed by cryogenic transmission electron microscopy on the colloidal phase. The colloids were collected in solid powder form by evaporating the continuous aqueous
35 phase. By X-ray diffraction, the diffractogram showed the presence of an LaMnO₃ phase.

EXAMPLE 2

This example relates to the preparation of an LaMnO_3 colloidal dispersion of small colloid size using
5 aminocaproic acid.

A manganese nitrate solution was obtained by dissolving 62.75 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (MW = 250.9, i.e. 250 millimoles of Mn) to which 500 cm^3 of demineralized
10 water was added. A lanthanum nitrate solution was obtained by diluting 146.5 g of a 2.88M La lanthanum solution of 1.686 density with demineralized water so as to obtain 500 cm^3 of solution (i.e. 250 millimoles).

15 The manganese nitrate solution was mixed with the lanthanum nitrate solution.

19.68 g of 6-aminocaproic acid ($\text{H}_2\text{N}(\text{CH}_2)_5\text{CO}_2\text{H}$, MW = 131.2, from Aldrich) were dissolved in 650 cm^3 of
20 a 3M aqueous ammonia solution. The aminocaproic acid/ LaMnO_3 molar ratio was 0.6.

The manganese nitrate/lanthanum nitrate solution thus obtained was quickly added, at room temperature, to
25 650 cm^3 of a 3M aqueous ammonia solution while stirring. A precipitate formed instantly. The pH of the suspension obtained was 9.0.

The suspension was centrifuged at 4500 rpm for 15 min.
30 The pellet obtained was taken up in 1000 cm^3 of demineralized water, and stirred for 30 min. After again centrifuging for 15 min, the solid obtained was dried at room temperature for 16 hours. The solid was then dried further at 60°C for 10 hours.

35 The product was calcined with a hold of 6 h at 550°C. The reaction was exothermic and produced a slight fly-off of the product.

After cooling, the perovskite structure LaMnO_3 (MW = 242) was determined by X-ray diffraction.

12 g of LaMnO_3 (50 millimoles) prepared as described
5 above were added to 75 cm³ of 2M acetic acid and the
mixture stirred for 20 min. The [acetic
acid]/[perovskite] molar ratio was 3.

The mixture was transferred into a Teflon (PTFE)
10 container inserted into a hydrothermal treatment cell
(Parr bomb). The hydrothermal treatment was carried out
at 160°C for 16 hours.

After cooling, the supernatant phase was removed. The
15 pellet was redispersed with stirring in 25 cm³ of
demineralized water. A colloidal phase and a solid were
obtained. Perfectly individual, monodisperse colloids
having a mean size of 10 nm were observed by cryogenic
transmission electron microscopy on the colloidal
20 phase.

The pH of the dispersion was 5.1. The colloids were
collected in solid powder form by evaporating the
continuous aqueous phase. By X-ray diffraction, the
25 diffractogram showed the presence of an LaMnO_3 phase.

EXAMPLE 3

This example relates to the preparation of a colloidal
30 dispersion of $\text{La}_{0.66}\text{Sr}_{0.33}\text{MnO}_3$ using lauric acid.

A manganese nitrate solution was obtained by dissolving
62.75 g of $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (MW = 250.9, i.e. 250
millimoles of Mn) to which 250 cm³ of demineralized
35 water was added.

A lanthanum nitrate solution was obtained by diluting
57.6 cm³ of a 2.88M La lanthanum solution of 1.686
density with demineralized water so as to obtain

200 cm³ of solution (i.e. 166 millimoles of La).

A strontium nitrate solution was obtained by dissolving 17.56 g of Sr(NO₃)₂ (MW = 211.6) so as to obtain 50 cm³ of solution (i.e. 83 millimoles of Sr).

The manganese nitrate solution and the strontium nitrate solution were mixed with the lanthanum nitrate solution.

10

The solution of the three nitrates thus obtained was added, at room temperature and at a controlled rate, to 650 cm³ of 2.43M 34% tetraethylammonium hydroxide (TEAOH) with stirring. The addition time was 30 min. A precipitate formed instantly. This was left to mature at room temperature for one hour.

The suspension was centrifuged at 4500 rpm for 15 min. The pellet obtained was taken up in 1000 cm³ of demineralized water and stirred for 30 min. The suspension was again centrifuged.

In parallel, 27.9 g of lauric acid in demineralized water were added and, after adjustment of the pH to 9, the mixture was adjusted to a volume of 225 cm³. The lauric acid/La_{0.66}Sr_{0.33}MnO₃ weight ratio was 0.50. The mixture was left for 16 hours with stirring.

The lauric acid solution was added to the pellet obtained above. The mixture obtained was milled in an Ultraturax mill for 15 min.

The product was calcined at 550°C for 6 h. A second calcination was carried out on the product in the following manner: the product was introduced quickly into a furnace preheated to 900°C and left there for 10 min. After this time, it was quickly removed.

XRD analysis on the product obtained showed that there

was mainly a single perovskite phase. The crystallite size determined by XRD was 22 nm.

2.79 g of $\text{La}_{0.66}\text{Sr}_{0.33}\text{MnO}_3$ (12.5 millimoles) prepared as described above were added to 25 cm³ of 2M acetic acid and stirred for 20 min. The [acetic acid]/[perovskite] molar ratio was 4.

The mixture was transferred into a Teflon (PTFE) container inserted into a hydrothermal treatment cell (Parr bomb). The hydrothermal treatment was carried out at 160°C for 16 hours.

After cooling, the supernatant phase was removed. The pellet was redispersed with stirring in 25 cm³ of demineralized water. A colloidal phase and a solid were obtained. Colloids having a mean size of 20 nm were observed by cryogenic transmission electron microscopy on the colloidal phase. The colloids were collected in solid powder form by evaporating the continuous aqueous phase. By X-ray diffraction, the diffractogram showed the presence of $\text{La}_{0.66}\text{Sr}_{0.33}\text{MnO}_3$.

EXAMPLE 4

This example relates to the preparation of a colloidal dispersion of LaFeO_3 .

A lanthanum nitrate solution was obtained by diluting 146.5 g of a 2.88M La lanthanum nitrate solution of 1.686 density with demineralized water so as to obtain 500 cm³ of solution (i.e. 250 millimoles). Next, 101 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (MW = 404, i.e. 250 millimoles of Fe) were added to this solution, which was left with stirring until the iron salt had completely dissolved.

The iron nitrate/lanthanum nitrate solution thus obtained was quickly added, at room temperature, to 550 cm³ of 3M aqueous ammonia solution while stirring. A precipitate formed instantly. The pH of the

suspension obtained was 9.0.

The suspension was centrifuged at 4500 rpm for 15 min. The pellet obtained was taken up in 1000 cm³ of demineralized water and stirred for 30 min. The suspension was again centrifuged for 15 min and the solid obtained was dried at room temperature for 16 hours. The solid was dried further at 60°C for 10 hours.

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The product was calcined at 650°C for 6 h.

After cooling, it was determined by X-ray diffraction that the product had an LaFeO₃ (MW = 243) perovskite structure.

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4.03 g of LaFeO₃ (16.5 millimoles) prepared as described above were added to 25 cm³ of 0.5M acetic acid and the mixture stirred for 20 min. The [acetic acid]/[perovskite] molar ratio was 0.75.

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The mixture was transferred into a Teflon (PTFE) container inserted into a hydrothermal treatment cell (Parr bomb). The hydrothermal treatment was carried out at 80°C for 16 hours.

25

After cooling, the supernatant phase was removed. The pellet was redispersed with stirring in 25 cm³ of demineralized water. A colloidal phase and a solid were obtained. Colloids having a mean size of 35 nm were observed by cryogenic transmission electron microscopy on the colloidal phase. The colloids were collected in solid powder form by evaporating the continuous aqueous phase. By X-ray diffraction, the diffractogram showed the presence of an LaFeO₃ phase.

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EXAMPLE 5

This example relates to the preparation of a colloidal dispersion of LaCoO₃.

A lanthanum nitrate solution was obtained by diluting 146.5 g of a 2.88M La lanthanum solution of 1.686 density with demineralized water so as to obtain 5 500 cm³ of solution (i.e. 250 millimoles). 72.75 g of Co(NO₃)₂·6H₂O (MW = 291.03, i.e. 250 millimoles of Co) were added to this lanthanum nitrate solution. This was left with stirring until the cobalt salt had completely dissolved.

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The cobalt nitrate/lanthanum nitrate solution thus obtained was quickly added, at room temperature, to 630 cm³ of 2M sodium hydroxide solution. A precipitate formed instantly. The pH of the suspension obtained was 15 11.6.

The suspension was centrifuged at 4500 rpm for 15 min. The pellet obtained was taken up in 1000 cm³ of demineralized water and stirred for 30 min. The 20 suspension was again centrifuged for 15 min and the solid obtained was dried at room temperature for 16 hours. The solid was further dried at 60°C for 10 hours.

25 The product was calcined by introducing it directly into a furnace maintained beforehand at 1000°C. The calcination time was 1 min 30 s and the product was then quickly removed from the furnace.

30 After cooling, it was determined by X-ray diffraction that the product had mainly an LaCoO₃ (MW = 246) perovskite structure with a minor amount of La₂CO₅ phase.

35 4.92 g of LaCoO₃ (20 millimoles) prepared as described above were added to 25 cm³ of 0.1M acetic acid and the mixture stirred for 20 min. The [acetic acid]/[perovskite] molar ratio was 0.2.

The mixture was transferred into a Teflon (PTFE) container inserted into a hydrothermal treatment cell (Parr bomb). The hydrothermal treatment was carried out at 80°C for 16 hours.

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After cooling, the supernatant phase was removed. The pellet was redispersed with stirring in 25 cm³ of demineralized water. A colloidal phase and a solid were obtained. Colloids having a mean size of 25 nm were
10 observed by cryogenic transmission electron microscopy on the colloidal phase. The colloids were collected in solid powder form by evaporating the continuous aqueous phase. By X-ray diffraction, the diffractogram showed the presence of an LaCoO₃ phase.

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EXAMPLE 6

This example relates to the preparation of a colloidal dispersion of LaMnO₃ whose colloids are anisotropic.

20 1) Firstly, an anisotropic perovskite was prepared in the following manner.

Added to a beaker were 4.225 g of MnSO₄·H₂O (MW = 153, i.e. 27mM of Mn) and 17.1 g of ammonium persulfate
25 (NH₄)₂(S₂O₈) (MW = 228, i.e. 75mM) in a 50 ml volume by addition of distilled water. The mixture was stirred until the salts had completely dissolved.

The solution was poured into a Teflon (PTFE) container.
30 of an autoclave (Parr bomb). The assembly was then heated for 16 hours at 140°C.

The solid obtained was recovered by centrifugation and then contacted with 300 ml of 1M NH₄OH solution. This
35 was left with stirring for 2 hours and centrifuged again. The solid was washed with 300 cm³ of demineralized water adjusted to pH 7 by an HNO₃ solution. The solid was recovered by centrifugation and left to dry at room temperature for 48 hours. The X-ray

diffraction spectrum showed the presence of an α - MnO_2 structure. Anisotropic objects of the fiber type ($L = 0.500 \mu\text{m}$; $I = 0.020 \mu\text{m}$) were observed by transmission electron microscopy.

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10 g of this α - MnO_2 powder were then impregnated using the dry impregnation technique with an $\text{La}(\text{NO}_3)_3$ solution. Thus, 28 cm^3 of $\text{La}(\text{NO}_3)_3$ solution comprising 0.51M of La^{3+} were added to 10 g of α - MnO_2 and mixed using a spatula until a paste was obtained. This was left to dry at room temperature overnight and then calcined at 650°C for 6 hours. This impregnation operation was repeated until an (La/Mn) molar ratio of 1 was obtained. The formation of the LaMnO_3 phase was confirmed by XRD. Anisotropic fibers of length $L = 0.5 \mu\text{m}$ and width $l = 0.02 \mu\text{m}$ were observed by transmission electron microscopy.

20 2) Next, a dispersion according to the invention was prepared in the following manner.

25 10 g of LaMnO_3 and 40 ml of 1M acetic acid were placed in a Parr bomb. The acid/perovskite molar ratio was 1. The assembly was heated for 16 hours at 140°C . After being centrifuged, the solid was reslurried with demineralized water to 120 ml. The supernatant phase was colloidal and contained LaMnO_3 fibers of dimensions $L = 0.5 \mu\text{m}$ and $l = 0.02 \mu\text{m}$.